2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
***ISBN:* 978-85-99141-05-2**

DESULFURIZATION OF PETROLEUM INDUCED BY IONIZATION RADIATION: BENZOTHIOPHENE BEHAVIOR

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Hydrodesulfurization (HDS) is currently the most common method used by refineries; this removes significantly sulfur compounds from petroleum fractions, however, is not highly effective for removing thiophenes compounds such as benzothiophene, and generates high costs for the oil industry. Another factor, are the environmental laws, which over the years has become increasingly strict, especially regarding the sulfur content. This compound cause incalculable damage both to the industry and to the environment. Therefore new methods for petroleum desulfurization should be studied in order to minimize the impacts that these compounds cause. In the present study it was used ionizing radiation, a promising method of advanced oxidation in reducing sulfur compounds. The analysis were performed after purge and trap concentration of samples, followed by gas chromatography-mass spectrometry (GC-MS). Then benzothiophene samples with the same concentration from 27 mg.L^{-1} to 139 mg.L^{-1} were irradiated with different absorbed doses of radiation ranging from 1 kGy to 20 kGy in gamma irradiator Cobalt-60, Gammacell. These samples were analyzed by the same procedure used for the calibration curve, and the removals of benzothiophene after ionizing radiation treatment were calculated. It was observed that at higher doses there was a greater degradation of this compound and the formation of fragments, such as 1,2-dimethylbenzene and toluene, which may be removed by simple processes.

Keywords: benzothiophene, ionizing radiation, advanced oxidation

1. Introduction

Sulfur compounds are present in almost all fraction of petroleum, and are undesirable compounds. The problem generate by sulfur compounds are related with its concentration that affect the quality of the final products and the price. At refinery, cause corrosion of metals part, catalyst poisoning, cost with process to extract it from crude oil and products. There is also environmental problem, like acid rain, caused by oxidation of sulfur compounds to $SO_{x.}$ Nowadays the stringent environmental laws to decrease sulfur concentration in petroleum and derivatives have contributed to the search for technologies of treatment (Malvesti, 2009).

Hydrodesulfurization, HDS, is one of the currently methods used by petroleum industries to reduce the content of sulfur, it removes significantly the sulfur compounds, but it demands high loads of energy, since it’s necessary high temperatures, around 300-430ºC, and high pressure reaching $2x10^7$ Pa. In addition the high hydrogen consumption and the expensive catalysts are disadvantages of the process. Furthermore HDS process is efficient on removal of thiol, sulfide and disulfide, but it is not effective on removal of thiophene compounds. By these reasons, studies have been carried out applying ionizing radiation as advanced oxidation process to removal sulfur compounds, that has shown to be a promising method (Hernandez-Maldonado et al, 2005; Qu, 2007).

Some researchers have demonstrated that the radiation process can reduces the quantity of mercaptans, disulfides and sulfides from the heavy oil products. Sulfoxides and sulfones are generated as a result of the molecular transformation caused by oxidation induced by radiation. In other studies, electron beam associated with ozone reduces sulfur content in a heavy oil sample and the formed sulfones, which were removed after by simple process (National Energy Technology Laboratory, 2006; Zaykin, 2007; Zaykina, 2004).

The use of radiation ionization to reduce sulfur content in petroleum is not completely consolidate, therefore the present work aims to contribute to the development of this technology, studying the radiation interaction with benzothiophene, BT, which is present in three of the most important transportations fuels, that are gasoline, diesel and aviation kerosene, furthermore BT is one of the sulfur compounds that aren't efficiently removed from fuels by HDS process.

2. EXPERIMENTAL

2.1 Materials

The commercial reagent used in this investigation was BT, from Merck Inc. It was prepared a standard solution with 1391.6 mg.L^{-1} in methanol. From this standard it was prepared a 50 mL of work solution diluted in distillated water. By the dilution of this solution it was prepared calibration curve and samples for irradiation, which the highest concentration was 139.2 mg.L^{-1}.

2.2 Radiation Processing

The gamma irradiation was carried out at room temperature using a Cobalt-60 gamma irradiator, Gammacell type, at dose rate 1,45 kGy/h. All the irradiations were performed in a batch system and the delivered doses were 1kGy, 2 kGy, 3 kGy, 4 kGy, 5 kGy, 10 kGy, 15 kGy and 20 kGy. The Dosimetry Research Group calibrates this system routinely with Fricke dosimeter to determine the absorbed dose rate. The 20 mL vials were completely filled without headspace in triplicate.

2.3 Chemical Analysis

After irradiation the BT content in the samples were analyzed using an O.I Analytica 4560 Purge and Trap Sample Concentrator to separate and concentrated volatile organic compounds, VOC, from water. The sample (5ml) is placed in a closed chamber and a purge gas (helium) passes through the sample, carrying the VOC to the trap, where they are retained by the sorbents. By the end of the purge, the trap is heated in order to desorbs the compounds that are then injected onto the gas chromatography column coupled with mass spectroscopy from Shimadzu GC/MS-QP5000. The samples were injected onto a fused silica capillary column (30 m x 0.25 mm i.d., film thickness 0.25 µm) coated with DB-5. Helium was the gas carrier at a constant velocity of 42 cm/s. The temperature program was started at 30ºC programmed to100ºC at 10ºC/min and then programmed to 300ºC at 15ºC/min. The mass spectrometer was operated in the electron impact mode at 70KPa. The injector and interface temperatures were held at 250 and 230ºC, respectively.

3. RESULTS AND DISCUSSION

In Figure 1 is presented the calibration curve of BT diluted in water. The calibration curve was obtained with a regression coefficient of 0.9944, and the obtained experimental variability (N=10), expressed as standard deviation, was 10% .

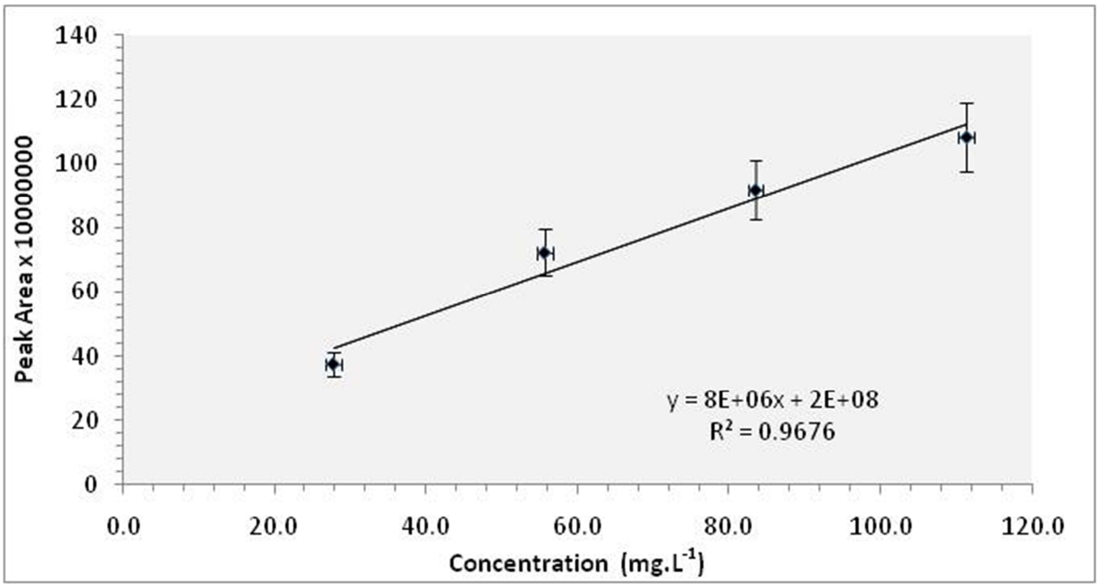


Fig1. Benzothiophene calibration curve obtained at MSGC after purge and trap concentration

After irradiation the samples were analyzed to quantify the BT, and the removals in function of absorbed dose were calculated. In Figure 2 is presented the graphic of BT removal (%) in function of the absorbed doses (kGy). The efficiency of this oxidation process is related with the increase of radiation dose (Fig. 2). The results show that almost the totality of BT was removed with 20kGy.

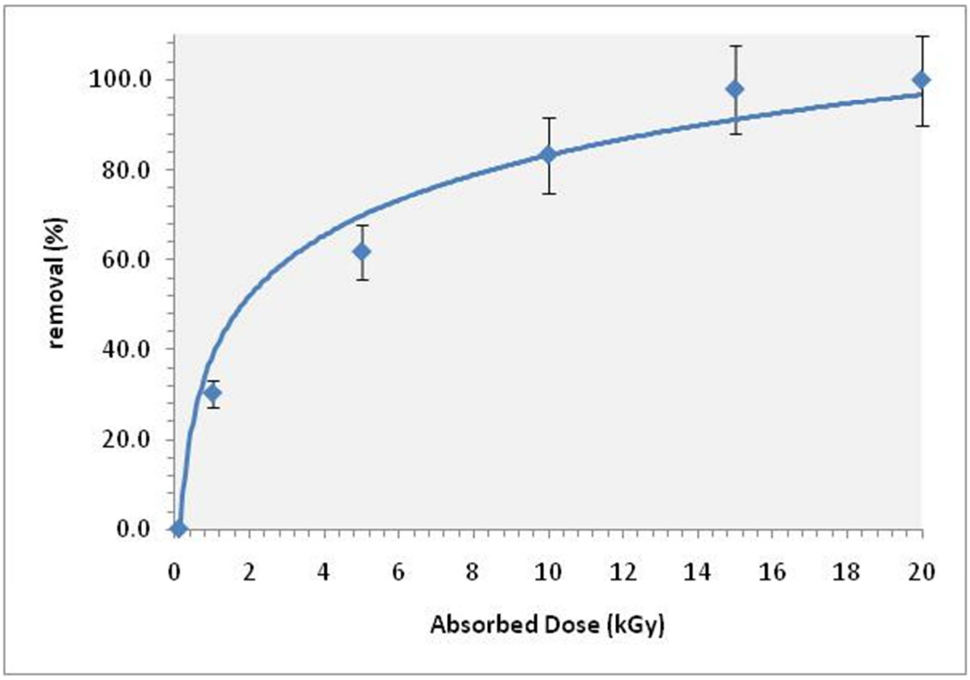
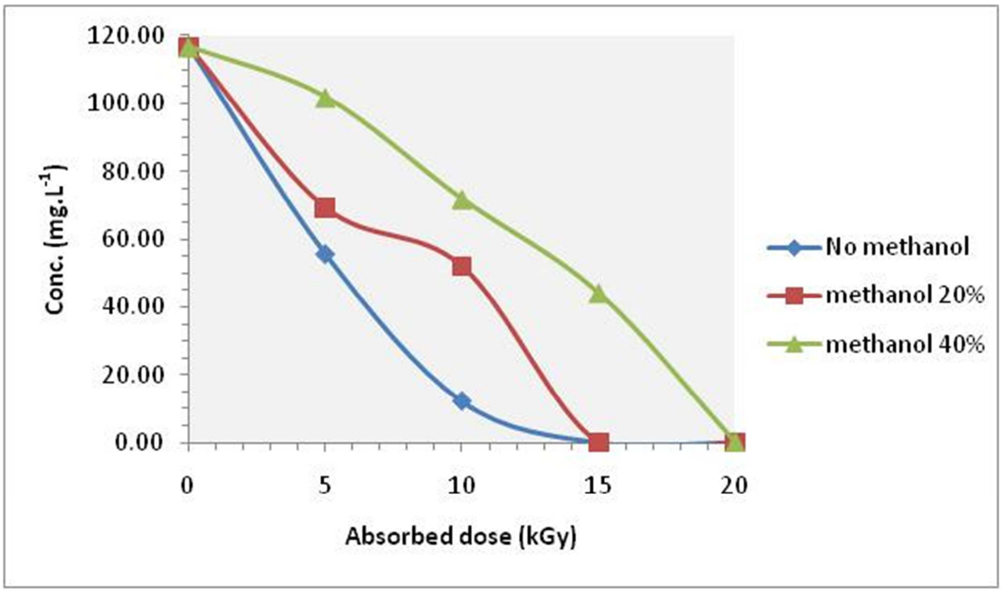


Fig.2 Benzothiophene removal efficiency different radiation doses

It was also observed the formation of some other fragments such as benzothiophan, thiophen, toluene and dimethylbenzene. The sulfoxides and sulfone groups were not identified by GC/MS method.

3.1 Methanol effect

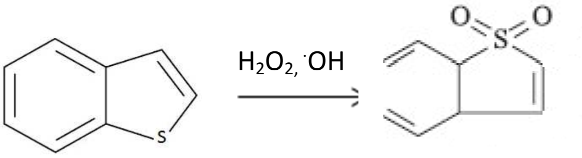
Another assay with benzothiophene diluted in water was made with the addition of methanol 20%, 40%, and 60% were irradiated with 5 kGy, 10 kGy, 15 kGy and 20 kGy. The results of removal of BT in function of absorbed dose are presented in Figure 3. With the addition of 60% of methanol and dose of 20 kGy the removal is not significant, that maybe happens because the radicals produced by the water radiolysis react preferentially with the OH of the methanol oxidizing it, but with the addition of 20 % of methanol the removal is efficient.



The presence of water directly affects the efficiency of the irradiation process; it is known that water suffers decomposition into of hydrogen atoms and hydroxyl radicals with radiation, which are illustrated in Eqs. (1-2), these radicals react with BT. The possible mechanism for BT oxidation were proposed as follows Eq.(3), also from de literatures it is believed that BT oxidizes to sulfoxide and sulfone groups (Duarte,1999; Qu, Z., 2007)

$$H_2O \longrightarrow H^{\bullet}, {}^{\bullet}OH, H_2, H_2O_2 \qquad (1)$$

$$2\,{}^{\bullet}OH_2 \longrightarrow H_2O_2 + O_2 \qquad (2)$$



(3)

4. CONCLUSION

There was a high efficiency on the removal of benzothiophene compound, demonstrating that it is possible to use ionizing radiation as an oxidative process, which can be associated with the HDS process, aggregating benefits, due to cost reduction. The products generated can be removed by simple processes well known by the petroleum industries.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of CAPES.

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